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Book Review

Asymmetric Organocatalysis: From Biomimetic Concepts to Applications in Asymmetric Synthesis By Albrecht Berkessel (Universität zu Köln, Germany) and Harald Gröger (Service Center Biocatalysis, Hanau-Wolfgang, Germany). Wiley-VCH Verlag GmbH & Co. KgaA: Weinheim, Germany. 2005. xiv + 440 pp. $195.00. ISBN 3-527-30517-3.

Merritt B. Andrus

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BOOK REVIEWS

What is What in the Nanoworld: A Handbook on Nanoscience and Nanotechnology. By Victor E. Borisenko (Belarusian State University, Minsk, Belarus) and Stefano Ossicini (University of Modena and Reggio Emilia, Emilia, Italy). Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany. 2004. xii + 336 pp. $190.00. ISBN 3-527-40493-7.

This reference provides definitions for important terms in nanoscience and nanotechnology, arranged in alphabetical order. In addition to a definition, where appropriate, more information about where the term was first described and where to find more information are provided. A listing of sources of information, including Web sites, is provided at the beginning of the book and an appendix of tables entitled “Main Properties of Intrinsic (or Lightly Doped) Semiconductors” completes it.

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Asymmetric Organocatalysis: From Biomimetic Concepts to Applications in Asymmetric Synthesis. By Albrecht Berkessel (Universität zu Köln, Germany) and Harald Gröger (Service Center Biocatalysis, Hanau-Wolfgang, Germany). Wiley-VCH Verlag GmbH & Co. KgaA: Weinheim, Germany. 2005. xiv + 440 pp. $195.00. ISBN 3-527-30517-3.

The past few years have witnessed a significant new movement in organic synthesis: the use of small organic, metal-free compounds as catalysts for an ever-widening range of asymmetric transformations. The term “organocatalysis” has been aptly coined for this new approach, which is an alternative to the use of traditional metal−ligand complexes and biocatalytic enzymes that have previously been developed. Robust, highly effective organocatalysts are typically inexpensive, like proline—which is often used alone—and other amino acids, cinchona alkaloids, etc., that are readily available from simple chiral feedstocks. Initially, only a few specific examples were known, but since 2000, the field has rapidly expanded as our understanding of catalytic design, substrate activation, and mechanistic considerations has begun to unfold. Industrial applications of organocatalysis, which lag behind academic investigations at this time, will certainly increase as key advantages, such as cost, stability, reuse, and generality, become more widely disseminated and appreciated. In the midst of this organocatalytic revolution comes this first book dedicated to the field, which now serves as a repository of past efforts as well as an important instructional tool to those unfamiliar with the area. It nicely covers all the important reactions of the area, including nucleophilic substitution on various functional groups, cycloadditions, oxidations, reductions, and various kinetic resolutions. Key papers, while not exhaustive, are well covered through late 2004.

The authors have wisely organized this book by the type of reaction, focusing on the reactive intermediate and its relation with the substrate and catalyst. This allows for an examination of the intermediates currently available in organocatalysis and an appreciation of the broadening scope of the process. All the key examples that have provided impetus to the field are well presented, including (a) glycine alkylation for amino acid synthesis using cinchona alkaloids as phase-transfer catalysts, (b) the Hajos−Parrish−Eder−Wiechert−Sauer intramolecular aldol process catalyzed by proline and its more recent development to include intermolecular examples and Mannich applications, (c) allyl additions and aldol reactions with phosphoramides, (d) hydrocyanation of imines and aldehydes using cyclic dipeptides and urea-based Schiff base catalysts, (e) chiral dioxiranes for unactivated epoxidation of alkenes, (f) oxazaborolidines for reductions of ketones, and (g) the resolution of alcohols using chiral phosphines.

More current contributions to the field are also amply covered. These include the recent influential work of MacMillan, who has pioneered the use of oxazolidinone catalysts for the formation of transient iminium and enamine species, which has led to an impressive range of useful Diels−Alder and 3 + 2 cycloadditions, Michael additions, conjugate additions with heterocyclic aromatics, and halogenations. The success demonstrated by his group in particular demonstrates the utility of focusing on the nature of the reactive intermediate, as opposed to a particular reaction type, and serves to firmly establish the field as a legitimate alternative to the use of metal complexes and enzymes. The authors also cover halogenation, including fluorination, incorporation of chlorine and bromine via in situ ketene formation, as well as the reaction of ketenes with imines to generate lactams under convenient organocatalytic conditions. The novel chiral ferrocenes developed by Fu, the peptides designed by Miller for highly useful kinetic resolutions of racemic alcohols, and the work of Deng using cinchona catalysts for efficient desymmetrizations are also discussed. Other reactions that are described include additions to diazo and nitroso compounds, aldehyde alkylation, tautomerization of enols, β-lactone synthesis, the Darzens, Horner−Wadsworth−Emmons, and Morita−Baylis−Hillman reactions, epoxidation of electron-deficient alkenes and aldehydes, sulfoxidation, aziridinations, kinetic resolution via alcohol oxidation, and the Benzoin and Stetter reactions using *N*-heterocyclic carbene catalysts. A chapter on industrial applications and a useful chart of specific catalysts together with their various uses are found at the end of the book.

The book is well written with clear, focused schemes that allow the reader to become readily immersed in the topics. Unifying principles and applications are clearly identified, which should facilitate future efforts toward the development of new substrates, reactions, conditions, and design of catalysts. As progress in the field continues to accelerate, this book will be

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of great value to those involved in synthetic methodology, catalysis, and total synthesis.

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Fundamental World of Quantum Chemistry: A Tribute to the Memory of Per-Olov Löwdin, Volume III. Edited by Erkki J. Brändas (Uppsala University, Sweden) and Eugene S. Kryachko (Bogoliubov Institute for Theoretical Physics, Kiev, Ukraine, and University of Leuven, Belgium). Kluwer Academic Publishers: Dordrecht, The Netherlands. 2004. xlvi + 677 pp. $225.00. ISBN 1-4020-2583-1.

This is the third volume in a series dedicated to the memory of Per-Olov Löwdin's pioneering and limitless efforts to found and establish the science of quantum chemistry. Volumes I and II were reviewed previously in this journal (Boyd, R. J. *J. Am. Chem. Soc.* **2004**, *126*, 6836).

Löwdin (1916−2000) was one of a special group of legendary figures of the past century who made immeasurable contributions to the discipline of quantum chemistry through his seminal publications on a remarkable diversity of topics. His legacy, however, is much greater than the sum of his publications. He established the Uppsala Quantum Chemistry Group in 1955 and the Quantum Theory Project at the University of Florida in 1960. Under Löwdin's leadership, the Uppsala and Gainesville groups rose quickly to rank among the three or four most influential theoretical groups in the world. In 1958, he organized the first of his famous Summer Schools in Sweden, and in 1961 he founded the Sanibel Symposia, which continue to be held annually. Through the organization of nearly 70 Summer Schools, Winter Institutes, and Sanibel Symposia, Löwdin had an inestimable effect on the careers of thousands of scientists. This reviewer still has his notes from the 1968 Winter Institute in Gainesville. I fondly recall his remarkable lectures, which I heard as a young graduate student. The first lecture began on a philosophical note in which he outlined the "tree of science" and then proceeded to a *tour de force* summary of the history of quantum theory. Later he gave an equally impressive lecture on quantum biology in the Winter Institute. Few scientists have achieved such a commanding overview of science. His perspective was no doubt influenced by the reading and preparation he did for the sessions of the Nobel Prize committee.

Volume III is a worthy companion to the earlier volumes. The 28 contributions cover a broad range of topics, most of which make a direct connection with Löwdin's scientific contributions. Hall's brief personal reflections and assessment capture the essence of the polite Swedish gentleman and are a fitting complement to Shull's contribution in Volume I. The second chapter by André traces some aspects of the history of computational quantum chemistry and includes some comments on trends in the computer industry. The third chapter by Katriel is much more germane to Löwdin's interests, as is the fourth chapter by Burrows and Cohen. Both chapters are relevant to Löwdin's seminal studies of projection operator techniques and Lie algebra treatments, and both reference Löwdin's famous 1964 paper in *Reviews of Modern Physics*.

The remaining 24 chapters deal with a broad range of fundamental topics in quantum chemistry, including supersymmetry, superconductivity, relativistic quantum chemistry, time reversal symmetry, Löwdin's metric matrix, and an "appendix" to Löwdin's seminal series of papers on perturbation theory. The more chemically oriented chapters focus on solvation, bond dissociation energies, photodetachment energies, kinetic isotope effects, catalytic cycles, and a physical explanation for the periodic table of the elements. The majority of the chapters are surveys of the relevant background literature and include many recent references. Many of the authors, leaders in their own right, include personal tributes to Löwdin.

This volume, like the earlier two, provides a unique anecdotal record of the development of quantum chemistry and insight about one of its most engaging advocates. It is also a testament to the breadth and current status of the discipline, and a harbinger of some important problems that await the attention of future generations of researchers. For example, at the WATOC Congress in Toronto in 1990, Löwdin declared that "One of the most urgent problems of modern quantum chemistry is to treat the motions of the atomic nuclei and the electrons on a more or less equivalent basis."

Russell J. Boyd, *Dalhousie University*

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New Theories for Chemistry. By Jan C. A. Boeyens (University of Pretoria, South Africa). Elsevier B. V.: Amsterdam. 2005. xii + 280 pp. $170.00. ISBN 0-444-51867-3.

As with Boeyens' earlier volume, *Theories of Chemistry* (reviewed recently, *J. Am. Chem. Soc.* **2004**, *126*, 8350), this book is written for both graduate students and researchers who are interested in the foundations of chemical phenomena. The 2003 book, along with four reviews Boeyens wrote earlier, provides much of the mathematical and physical framework needed to understand the current text. Without this earlier monograph, or some other source for the contemporary mathematics and physics discussed, the reviewer is sadly convinced that many chemists will be at a loss for understanding the contents of this book, despite Boeyens' efforts at explaining and expanding upon his earlier writings. By titling the book *New Theories for Chemistry*, Boeyens acknowledges this: the word "new" correctly implies that the reader should understand the "old" and the "not-so-old", both the standard and the author's interpretation of the universe.

Words and concepts uncommon or unknown to most chemists abound. Calculational versatility aside, few chemists are familiar with the tenets, axioms, and corollaries of orthodox "Copenhagen" quantum theory. Bohm's alternative approach to the understanding of the universe, both more heretical and theoretical than most other modes and models of reality, is rarely practiced or understood by most chemists. Yet, this is the framework Boeyens finds necessary to use for much of the desired understanding. He may be right. My own informal and occasional exhortation paralleling Hillel and paraphrasing Dirac, "$H\psi = E\psi$. The rest is commentary", may well be wrong as well as far too simplistic. (Yes, I know one should quote the time-dependent Schrödinger equation.)

I was pleased to find three chapters on topics of profound chemical significance: chemical concepts, e.g., electronegativity, equilibrium, reaction, and bonding; molecular structure, e.g., diffraction methods and spectroscopy, chirality, rotational barriers, and molecular shape; and the chemical world—according to Boeyens, a very different place than that posited by most chemical theorists. There are numerous insights and comparisons with experiment. Some are interesting, some are provocative, and some are wrong. For example, I was bothered by such lines from the text as: “The progress of theoretical chemistry during the 20^{th} century was severely hampered by a misreading of quantum theory and relativity”; “The reason for this parallel alignment of the two separate atomic p_z orbitals is obscure. The illogical common explanation in terms of sideways overlap to form a π-bond, is almost like received dogma”; and “The dihydrogen molecule ... has no shape, no bond and, unless it interacts with external fields, no geometrical features.”

I was mildly troubled that some of the lines read as polemics. I was even more troubled by the chemical conclusions that arose from the author’s understanding of the universe. We are told ammonia has a valence shell consisting of three p-electrons—does Boeyens mean the nitrogen atom before molecular formation? We are told that B_2 and C_2 in their ground states have no and two unpaired electrons, respectively. The molecular spectroscopists tell us the opposite. BH_3 is described as having nonequivalent hydrogens; specifically, having a linear H−B−H with the remaining H perpendicular to this line. This is contrasted with BF_3. I recall both species being trigonal planar with 120° angles between the atoms attached to the central boron.

Boeyens discusses some additional topics such as the structures of the electron and of the nucleus, the dimensionality of space(−time), and the unification of electromagnetism and gravitation, and with this completely leaves chemistry. I now leave the book to the reader; for this reviewer, it was an interesting read and ride. Regrettably, $170 for a 280-page, photoreproduced hardcover book seems expensive for this experience.

Joel F. Liebman, *University of Maryland, Baltimore County*

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Targets in Heterocyclic Systems: Chemistry and Properties, Volume 7 (2003). Edited by Orazio A. Attanasi (University of Urbino) and Domenico Spinelli (University of Bologna). Italian Society of Chemistry: Rome. 2004. vi + 294 pp. $79.95. ISBN 88-86208-28.

“What’s in a name?” This was the question posed by Juliet in Shakespeare’s *Romeo and Juliet*, and the same question could be asked about this collection of short reviews compiled and edited by Attanasi and Spinelli. The collection is loosely based on the theme of heterocyclic chemistry and reflects the interests of the Italian authors of each chapter. Some of the chapters are concerned with the chemistry of various functional groups, whereas others focus on synthetic techniques (microwave, solid state) or methods of characterization (mass spectrometry).

Of the 11 chapters in this book, the first will have the most general audience appeal since it is a description of the regioselective opening of epoxides by various nucleophiles. This chapter is not a comprehensive review of the topic, but rather focuses on the applications related to the author’s personal research interests in the area. Overall, it is well written and thoroughly referenced, which is true for all of the chapters in this compilation.

Chapters 2, 4−7, 9, and 11 are descriptions of recent studies of isoxazol-5-ones, azapolycyclic indoles, oxathins, nitrones, the Paterno−Büchi reaction, 2*H*-azirines, and polynitro- and halonitrodihydrothiophene-1,1-dioxides, respectively. Many of these heterocyclic systems have a highly specialized following and may not be of interest to the wider community of heterocyclic chemists. With the exception of one or two chapters, the coverage is quite comprehensive.

Chapter 3 covers the application of microwave and solid-state synthetic techniques to the preparation of heterocyclic systems, particularly coumarins, and to the Diels−Alder reactions of furans. This chapter was disappointing because of the very limited coverage of this significant topic. The use of microwave synthetic methods in heterocyclic chemistry is very important, and a more comprehensive coverage would have been welcome. Chapter 8 on indoles and Chapter10 on 1,4-benzodiazepines are devoted to characterization of heterocyclic systems using mass spectrometry.

The major deficiency of this book is the lack of an index. Admittedly, the review format of the book mitigates the seriousness of this deficiency since the audience who will use this volume will most likely be reading specific chapters rather than using the book as a reference source. Nonetheless, no modern book should be published without an index. As noted above, the chapters are generally well referenced and current, including references through 2003. The overall quality of the binding and printing is good, although the paperback binding cannot be expected to withstand years of vigorous use. However, since this book is unlikely to serve as a text or reference source that will receive intensive use, the binding is adequate.

Philip DeShong, *University of Maryland*

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The Maillard Reaction: Chemistry, Biochemistry and Implications. By Harry Nursten (The University of Reading, Reading, U.K.). Royal Society of Chemistry: Cambridge. 2005. xii + 214 pp. $199.00. ISBN 0-85404-964-9.

The Maillard reaction is named in honor of Prof. Louis C. Maillard, who in 1912 reported on the brown color formed during heating of aldehydes and amines—not very exciting chemistry by modern standards, but certainly of lasting appeal. Last year, the 8th International Symposium on the Maillard Reaction marked the 25th anniversary of the Maillard Symposia. More than any other named reaction in organic chemistry, the Maillard reaction sparks interdisciplinary interest because it bridges the worlds of organic chemistry, food science, biochemistry, pathology, and gerontology. Unlike the other named reactions, the Maillard or browning reaction refers to a complex set of carbonylamine reactions with multiple mechanisms, pathways, and products. These reactions affect the color, taste, aroma, texture, nutritional value, and toxicity of foods during cooking. From the viewpoint of biochemists, Maillard reactions also proceed in the body at lower temperature (37 °C) for longer times (∼76 years). They contribute to the aging of tissue proteins, generation of oxidant stress, and development of pathology in chronic, age-related diseases, including cardiovascular and kidney disease, diabetes, and neurodegenerative diseases, such as Alzheimer's and Parkinson's diseases.

Nursten has been a student of the Maillard reaction for nearly half a century; he co-edited the Proceedings of the 6th International Maillard Symposium held in London in 1997. He has watched over and participated in the evolution of interest in this reaction, from the exclusive domain of food scientists and technologists to the growing interest of biomedical scientists. His book is not an edited volume, but a personal retrospective and perspective, providing both breadth of coverage and insight into the history and future of the Maillard reaction.

A brief historical introduction is followed by a concise chapter on the chemistry of reducing sugars: the Amadori rearrangement, Strecker degradation, aldol condensations, carbonylamine chemistry, etc., topics rarely covered in textbooks today. Here and throughout the book, Nursten presents excellent summaries of reaction pathways, characteristic products, and effects of reaction conditions. The Introduction is followed by discussion of the Maillard reaction in food chemistry, focusing on the effects of carbohydrates, lipids, and processing technology on food aroma, color, and taste. Chapters on toxicology and nutrition address the contrasting activities of Maillard products as mutagens, anti-mutagens, allergens, and antibacterial agents. These chapters provide a transition to discussions of the physiology and pathology of the Maillard reaction—its role in aging, kidney disease, and cancer—and then to other fields, including brief sections on soil science and textile chemistry. The final chapters deal with control or inhibition of the Maillard reaction in foods and living systems. The chapter on foods includes a section on “Six Main Ways to Inhibit Nonenzymic Browning”. Unfortunately, many of these, like dehydration, freezing, and addition of sulfites, will not work in living systems. Therefore, the last chapter deals with pharmacological approaches for inhibiting the Maillard reaction: the use of carbonyl trapping agents, antioxidants, enzymes, and hypoglycemic agents to inhibit or reverse the consequences of the Maillard reaction in vivo.

Although coverage is stronger in the areas of food science, technology, nutrition, and toxicology, the discussion of research on the Maillard reaction in biological systems is current and broad in scope. The bibliography includes more than 600 references, including seminal works in the field and leading research through 2004. *The Maillard Reaction* is a readable, concise history and overview of the field, an excellent laboratory resource, a “must read” for new students of the reaction, and a valuable resource for more senior scientists.

John W. Baynes, *University of South Carolina*

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Chemical Thermodynamics for Industry. Edited by T. M. Letcher (University of Natal, Durban, South Africa). Royal Society of Chemistry: Cambridge. 2004. xviii + 276 pp. $249.00. ISBN 0-85404-591-0.

This book follows the 1999 volume *Chemical Thermodynamics*, also edited by Letcher, but focuses more on applied thermodynamics in industry. Traditional areas, such as calorimetry, transport properties, and crystallization, to name a few, are covered as are more newly established areas, such as multiphase modeling, reactive distillation, nonequilibrium thermodynamics, and spectrocalorimetry. New and potentially important areas of research, such as ionic liquids, nanoparticles, clathrates, etc., are also described. There are 23 chapters, each written by leading experts in the topics covered, and a subject index.

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